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Effect of pretreatment method of activated carbon on the catalytic reduction of NO by carbon over CuO

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Abstract

The influence of pretreatment method of activated carbon (AC) made from coconut shell, on the NO reduction by AC over CuO was studied, in which AC was used as a reducing agent and pretreated by air oxidation or wet oxidation in the HNO_3(N), H_2O_2(H), H_2SO_4(S) or H_3PO_4(P) aqueous solution. The results show that over the CuO catalyst, the reductive activity of air oxidized AC for NO increases with a rise of the air oxidation temperature of AC, and the order of the reductive activity of wet oxidized AC for NO is AC-H > AC-N > AC-S > AC-P. The surface chemical properties of these ACs were studied by XRD, TPD, Boehm titration and so on. The dispersion of CuO on AC can be improved by treating AC with the HNO_3 or H_2O_2 aqueous solution. AC treated with H_2O_2 is an effective reducing agent for the reduction of NO over CuO, and the temperature of complete reduction of NO by AC-H is 270 °C, which is 120 °C lower than that by original AC. Both the high concentration of acidic oxygen groups and moderate amount of basic sites on AC-H help to increase the conversion of NO reduced by AC-H.

Keywords: Activated carbon; NO reduction; CuO catalyst; Surface treatment

1. Introduction

One of the not yet solved problems associated with air pollution is the purification of nitrogen oxides (NO_x) in waste gases. Due to their contribution to the rain acidification, photochemical smog, global warming and depletion of the stratospheric ozone layer, it has brought to the forefront of public concern [1,2]. In the interest of eliminating the emission of NO_x, several technologies or methods have been developed, of which the selective catalytic reduction (SCR) is the most considered one [2–10]. The SCR of nitric oxide by ammonia is currently the most widespread method for the clean-up of flue-gas from stationary sources. But stoichiometric control of ammonia must be maintained to avoid the emission of unreacted ammonia. Another problem of the SCR technology is the storage and transportation of ammonia. If activated carbon is used as the reducing agent instead of ammonia to reduce NO_x, the re-pollution of unreacted ammonia and the storage and transportation of ammonia can be avoided.

Activated carbon has a high surface area, bulk porosity and various surface chemical properties. It has been recognized as good adsorbent or support [11–16]. Using activated carbon as a catalyst for NO_x reduction with NH_3 [5], urea [6], CO [7,9] and C_3H_6 [8] as the reducing agents has drawn researchers' attention. Carbon-based catalysts offer significant advantages versus the conventional catalysts. For instance, there are various low price carbonaceous sources [17]. In the exhaust gases of stationary sources or lean-burn diesel engines there are a higher concentration of NO_x and large amounts of particulate matter that are mainly carbons and also called soot. Using the carbon particulates (soot) to reduce NO_x in the exhaust gas may be the most ideal method to remove NO_x, but the high effective catalysts must be used. In NO_x atmosphere, the catalytic removal of soot can be improved by the reaction of NO_2 and soot [18].

The adsorption capacity of AC is known to be a function of surface area, pore volume and porous structure. However, as a reducing agent, the surface chemical nature of AC plays an

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important role in the activity of carbon-based catalysts [12–16]. And the surface chemistry of AC can be changed by the interaction between the carbon surface and the reactants adsorbed, such as the treatment with oxidants (O_2, HNO_3, H_2O_2, $KMnO_4$, $(NH_4)_2S_2O_8$, $HClO_4$ and so on) [19–26]. H_2O_2 treatment can affect the surface chemistry of AC moderately and produce appropriate amount of the oxygen-containing complexes and surface acid groups. However, AC treated with H_2O_2 is seldom used to reduce NO_x.

In this paper, the catalytic reduction of NO by AC has been investigated over the CuO catalyst. The effect of H_2O_2 treatment of AC on the reduction of NO catalyzed by CuO catalyst has been studied. As a comparison, the treatments of AC with air, HNO_3, H_2SO_4 and H_3PO_4 were also carried out.

2. Experimental

2.1. Pretreatment of activated carbon

The parent activated carbon (AC) was supplied by Tangxin Activated Carbon Co. Ltd., Shanghai, and was prepared from coconut shells by carbonization under nitrogen and further activation with steam. Its BET surface area is 928 m^2/g with 1.79 wt% ash. AC was preoxidized in air at 300 °C, 400 °C or 500 °C for 6 h, which was labeled as 300AC, 400AC or 500AC. The wet oxidation of AC was carried out by impregnating AC in the aqueous solutions (2N) of HNO_3, H_2O_2, H_2SO_4 and H_3PO_4 for 48 h at room temperature with gentle shaking, respectively. The volume ratio of AC/solution is 1/5. Then, the samples were filtered and washed with de-ionized water to remove the remaining oxidants. The AC samples impregnated with the oxidation solution were treated in the stove at 400 °C for 4 h. Wet oxidized carbon samples were labeled as AC-N (treated with HNO_3), AC-H (H_2O_2), AC-S (H_2SO_4) and AC-P (H_3PO_4), respectively.

2.2. Preparation of the catalyst

The CuO catalyst was prepared by the wet impregnation method. AC was impregnated with aqueous solution of $Cu(NO_3)_2$ at room temperature for 4 h and aged at 60 °C for 2 h. After dried in air overnight at 110 °C, the CuO/AC samples were calcined in air at 250 °C for 4 h. The loading of CuO was 10 wt%, which was determined by burning off the carbonaceous supports.

2.3. Characterization of activated carbon and catalyst

N_2 adsorption isotherm, BET surface area and pore size distribution curve of sample were measured at −196 °C on a Micromeritics ASAP 2020 Sorptometer using static adsorption procedures.

X-ray diffraction (XRD) of sample was obtained on a Rigaku D/max-II/2550/VC X-ray powder diffractometer, Cu Kα radiation was employed and the working voltage and current were 40 kV and 100 mA, respectively.

Temperature-programmed desorption (TPD-MS) of sample was carried out in a quartz flow reactor (Ø 10 mm × 300 mm) system coupled to a quadrupole mass spectrometer (IPC400, INFICON Co. Ltd.). 200 mg sample was used, the flow of Ar was 100 ml/min, and the heating rate was 20 °C/min from 100 °C up to 900 °C.

The contents of acidic and basic sites on the surface of sample were determined by the Boehm method [27]. Each 500 mg sample was placed in 30 ml vial with 0.05N aqueous solutions of NaOH, Na_2CO_3, $NaHCO_3$ and HCl, respectively. After the vials were sealed and shaken for 24 h, the samples were filtrated and 10 ml filtrate was pipetted. Excessive NaOH or HCl were titrated with HCl and NaOH respectively. For the Na_2CO_3 and $NaHCO_3$ filtrate, 10 ml 0.05N H_2SO_4 was added and excessive H_2SO_4 was back-titrated with 0.05N NaOH after heated at 60 °C to boil off CO_2. The contents of acidic sites were calculated according to the assumption of the base solution, in which NaOH neutralizes the carboxylic, phenolic and lactonic or lactol groups, Na_2CO_3 neutralizes the carboxylic and lactonic or lactol groups, and $NaHCO_3$ neutralizes only carboxylic groups. The content of the surface basic sites was calculated by the amount of HCl reacted with the AC sample. After 1 g AC sample was immersed in 30 ml de-ionized water to reach equilibrium, the pH value of carbon suspension was determined by a pH meter according to the literature [20].

2.4. Testing of the catalytic reduction of NO by AC

Catalytic reduction of NO by AC was carried out at atmospheric pressure in a fixed bed microreactor (Ø 10 mm × 300 mm), the outlet gases were analyzed by two gas chromatographs (Fuli 9790) with two thermal conductivity detectors, and a column of Poropak Q for the separation of CO_2, N_2O, H_2O and a column of 5A zeolite for the separation of O_2, N_2 and CO. Five hundred milligrams catalyst was used, the space velocity (GHSV) was 20,000 h^{-1} and the concentration of NO in Ar was 2000 ppm. The reduction reaction of NO was studied using the procedure of temperature-programmed reaction (TPR) at a heating rate of 3 °C/min from 100 °C to 400 °C. In this reaction N_2 was the aim product, and N_2O was also formed but its concentration was very low and could be neglected. Therefore, the conversion of NO was calculated by the amount of nitrogen produced.

3. Results and discussion

3.1. Physicochemical properties of activated carbon

The pore structure properties of AC samples are shown in Table 1. The results show that the surface areas and total pore volumes of AC oxidized in air for 6 h increase with an increase in the oxidation temperature at <400 °C. After being oxidized at 500 °C for 6 h, the surface area and total pore volume of AC decrease appreciably. This may be resulted from the formation of some surface oxygen complexes at the entrance of pores. For the samples treated by the wet oxidation, the HNO_3 or H_2O_2